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**COSMETIC**  
[Keshoryo]

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## **Claims**

1. A cosmetic, characterized by comprising a sugar-fatty acid adduct selected from glucosamine, N-acetylglucosamine and homopolymers or copolymers thereof with degrees of polymerization of 10 or less.
2. The cosmetic according to Claim 1, wherein the sugar is obtained by the hydrolysis of chitin and/or chitosan.
3. The cosmetic according to Claim 1 or 2, wherein the average degree of fatty acid substitution in the sugars is 1 to 3.5.

## **Detailed explanation of the invention**

### **Industrial application field**

The present invention relates to a cosmetic, and in additional detail, relates to a cosmetic having excellent feel and properties during use, which contains specific sugar-fatty acid adducts that are used as oil gelling agents.

### **Prior art and its problems**

In the past, compositions having various configurations have been used in cosmetics, and various oil agents have been selected in accordance with the intended use of the cosmetic.

Among oil agents used in cosmetics, liquid oils such as hydrocarbon oils, ester oils and glyceride oils have a significant influence on the functional characteristics of cosmetics due to their specific properties. For example, if the liquid oil is light and smooth, then the cosmetic will likewise have a light feel, and will be easy to spread. For this reason, these liquid oils are blended with the objective of improving the functionality of cosmetics by improving their lightness and spreading properties when the cosmetic is

used. Moreover, liquid oils are almost never used alone in cosmetics, but are generally used together with other semisolid or solid oils and oil gelling agents, depending on the configuration and functionality of the cosmetic. In particular, with solid cosmetics, oils are blended with solid waxes and oil gelling agents as solidification agents in order to provide shape retention properties. These solidification agents are used because stability is improved when the substances are gelled or solidified, in contrast to when liquid oils alone are used. This allows the production of various configurations due to the capacity for shape retention, while also improving the properties of the cosmetic from the standpoint of practical use. There are numerous known solidification agents that are used toward these objectives, but examples of commonly used substances include oil gelling agents such as hydrocarbon-based solid waxes, starch-fatty acid esters and metal soaps.

In this connection, a light and refreshing feel when using a cosmetic is an important functional characteristic of the cosmetic, and in recent years in particular, there has been a trend in which these characteristics have become increasingly desired. Although substances with low molecular weights have been used as liquid oils, important considerations also include selection of the solidification agent in addition to the liquid oil agent. The use of a solidification agent that does not interfere with the properties of the liquid oil is also important.

However, although each of these conventional solidification agents is useful, they have various disadvantages, and an adequate agent has not been found. Specifically, when solid waxes are used, the cosmetic will have a hard feel, and will be heavy or difficult to spread. In addition, there have been cases where the liquid oil agent has separated out after molding into a solid. When using starch-fatty acid esters as oil gelling agents, on the other hand, extremely stable gelling is achieved. However, the molecular weight of the compound is high, which leads to effects that are manifested in the cosmetic. As a result, even if a liquid oil having a smooth and light feel is used, a thick filmy or fatty, tacky feel will result after

application of the cosmetic layer. Moreover, when metal soaps are used, gelling does not reliably occur.

As a result, the liquid oil agent tends to separate out, so that use of these agents alone is problematic.

Although liquid oil agents are desirable from the standpoint of use objectives, there is significant variation in feel and stability in the resulting cosmetic due to the solidification agent, and it is thus difficult to produce a cosmetic that is satisfactory in this regard. For this reason, demand is increasing daily for the development of a solidification agent that does not have a detrimental influence on liquid oil properties, while also being favorable from the standpoint of cosmetics.

#### Means to solve the problems

The inventors of the present invention, et al., carried out painstaking investigations in light of this state of affairs. The present invention was thus perfected, based on the discovery that fatty acid adducts obtained by the addition of fatty acids to specific sugars exhibit excellent performance as oil gelling agents, and that cosmetics that contain these compounds have superior feel and properties during use, as well as superior stability.

Specifically, the present invention is a cosmetic, characterized by comprising sugar-fatty acid adducts selected from glucosamine, N-acetylglucosamine and homopolymers or copolymers thereof having degrees of polymerization of 10 or less.

The sugars used in the present invention are sugars that are selected from glucosamine, N-acetylglucosamine, homopolymers thereof with average degrees of polymerization of 10 or less, or copolymers wherein the two are randomly distributed linearly via  $\beta$ -1,4 linkages. Among these substances, hydrolysis products of chitosan and/or chitin with average degrees of polymerization of 10 or less are particularly desirable. These compounds can be readily obtained by a hydrolysis reaction carried out using a conventional well-known method involving natural macromolecular chitin, which is contained in large

quantities in crustaceans, arthropods and the like. For example, a method can be used that involves treatment with concentrated hydrochloric acid, followed by neutralization and desalting, or a method can be used that involves the use of enzymes. A deacetylation reaction can then be carried out, as necessary, by treatment with concentrated alkali.

If the average degree of polymerization of the sugars is 11 or greater, it will be difficult to dissolve the substance in the liquid oil agent, and good gelling will not occur. Consequently, the average degree of polymerization is preferably 10 or less.

The type of fatty acid that is to be added to the sugars depends on the average degree of polymerization of the sugars and the amount of added fatty acid, so that a universally valid prescription cannot be given. However, compounds with carbon numbers in the range of 8-22 are preferred, and examples that may be cited include palmitic acid, stearic acid, oleic acid, isopalmitic acid and isostearic acid.

When adding fatty acid to the sugars, compounds can be readily obtained by well-known methods involving ester bonding and amide bonding. For example, the sugars can be dispersed in pyridine, fatty acid halide or fatty acid anhydride can be added, and a 2-8 h reaction can then be carried out at about 100°C. The added amount of fatty acid halide or fatty acid anhydride, as well as the reaction time and reaction temperature, can be selected appropriately in order to control fatty acid addition. In the present invention, the added amount of fatty acid with respect to the sugars has no particular restrictions, but compounds in which an average of 1-3.5 molecules of fatty acid are added per single sugar unit in the sugars are preferred. Compounds with addition levels in this range have particularly desirable gel formation capacity. The sugar-fatty acid adduct can be obtained as a white to brown powder, depending on the reaction conditions. However, the brown powder can be easily purified, if necessary, to form a white powder using conventional well-known decolorization methods, such as treatment with activated carbon, Celite, or other such material.

The sugar-fatty acid adduct obtained in this manner has excellent performance as an oil gelling agent. After heating and dissolving the substance together with the liquid oil agent used in the cosmetic, the material readily brings about gelling when cooled, thus forming a gel-form or solid material with favorable shape retention and feel during use. At this time, gelling or solidification can occur, regardless of the type of liquid oil agent, e.g., hydrocarbon oil, ester oil, or glyceride oil.

The cosmetic of the present invention can be manufactured by blending the aforementioned sugar-fatty acid adducts using common methods. For example, sugar-fatty acid adduct and liquid oil agent or oil containing liquid oil agent may be blended and heated to dissolve the substances, thus preparing a preliminary gel-form or solid composition. Subsequently, this composition can be blended with other cosmetic components, and dissolved or dispersed to produce the cosmetic. In addition, the blend amount of sugar-fatty acid adduct will be different, depending on the type and objective of use of the cosmetic. Although there are no particular restrictions on the blend amount, the amount is 5-50 wt% for solid cosmetics, with 7-30 wt% being preferred. At amounts that are less than 5 wt%, a good gel-form or solid-form cosmetic will be difficult to obtain, whereas amounts in excess of 50 wt% are undesirable because the cosmetic will be too hard.

Components that are used in other common cosmetics, such as oils other than those mentioned above, white pigments, extender pigments, colorant pigments, organic powders, pearlescent agents, tar dyes, surfactants, macromolecular compounds, gelling agents other than those mentioned above, ultraviolet absorbers, antioxidants, preservatives, polyhydric alcohols, fragrances, and beautifying agents, may be appropriately selected and used. In addition, the composition may be used for various cosmetics such as a foundation cosmetic, make-up cosmetic or hair cosmetic.

## Application examples

Reference examples and application examples are presented below in order to describe the present invention, but the present invention is not in any way restricted by these examples.

## Reference examples

The sugar-fatty acid adducts manufactured by the methods described below were used as samples.

### Sample (1)

5 g of N-acetylglucosamine (Sigma) were added to 55 mL of pyridine, and the mixture was heated to 100°C while stirring. 12 g of stearic acid chloride were then added dropwise, and a reaction was allowed to occur for 3 h. After completion of the reaction, the pyridine was evaporated off, and the material was washed with about 50 mL of methanol. The product was then dried for 10 h under reduced pressure at 50°C to obtain 8.5 g of brown powdered product. The degree of acid substitution of the product (expressed as the number of molecules of fatty acid added per sugar unit in the sugar; likewise below) was 1.01, as determined by elemental analysis.

### Sample (2)

5 g of glucosamine (Sigma) were added to 55 mL of pyridine, and the mixture was heated to 100°C while stirring. 12 g of stearic acid chloride were then added dropwise, and a reaction was allowed to occur for 3 h. Upon completion of the reaction, the pyridine was evaporated off. After washing with about 50 mL of methanol, the product was dried for 10 h under reduced pressure at 50°C to obtain 9.1 g of brown powdered product. The degree of acid substitution of the product was 1.08, as determined by elemental analysis.



### Sample (3)

380 g of 6N hydrochloric acid were added to 20 g of chitosan with a molecular weight of about 180,000 and a deacetylation level of 80%, and a hydrolysis reaction was allowed to occur while stirring for 6 h at 70°C. Upon completion of the reaction, 400 mL of water were added to dilute the solution, and the mixture was filtered to remove the insoluble matter. The filtrate was then subjected to vacuum concentration using a rotary evaporator, and the solidified powder that was obtained was extracted with methanol. The soluble component was then dried to obtain 6.0 g of chitosan hydrolysis product with a degree of polymerization of 0-5, and a primary degree of polymerization of 2-3.

Next, 5 g of said hydrolysis product were added to 55 mL of pyridine, and the mixture was heated to 100°C while stirring. 12 g of palmitic acid chloride were then added dropwise, and a reaction was allowed to occur for 3 h. Upon completion of the reaction, the pyridine was evaporated off, and after washing with about 50 mL of methanol, the material was dried under reduced pressure for 10 h at 50°C to obtain 9.5 g of brown powdered product. The fatty acid substitution level of the product was 1.16, as determined by elemental analysis.

### Sample (4)

190 mL of concentrated hydrochloric acid were added to 10 g of chitin having an average degree of polymerization of 500,000 and a degree of acetylation of 12%. A hydrolysis reaction was then allowed to occur while stirring for 2 h at 40°C. Upon completion of the reaction, the solution was neutralized with 1N sodium hydroxide, and was filtered to remove the insoluble matter. The filtrate was then passed through an activated charcoal-celite column with an inner diameter of 4.4 cm and a length of 100 cm thus effecting adsorption of the target substance. After adsorption, the column was washed with 2 volumes of water

relative to the filtrate, and 200 mL of 30% ethanol solution were then run through the column in order to elute the target product. Said solution was then subjected to vacuum concentration at 50°C in an evaporator, and was dried to obtain 3.0 g of chitin hydrolysis product with a degree of polymerization of 1-5, but primarily 2-3.

2 g of said hydrolysis product were then added to 22 mL of pyridine and heated to 100°C while stirring. 4.8 g of stearic acid chloride were then added dropwise, and a reaction was allowed to occur for 3 h. Upon completion of the reaction, the pyridine was evaporated off, and after washing with about 20 mL of methanol, the solution was dried for 10 h at 50°C under reduced pressure to obtain 3.6 g of a brown powdered product. The fatty acid substitution level of the product was 1.05, as determined by elemental analysis.

#### Sample (5)

5 g of N-acetylglucosamine (Sigma) were added to 55 mL of pyridine, and while stirring, the mixture was heated to 100°C. After dropwise addition of 26 g of stearic acid chloride, a reaction was allowed to occur for 3 h. Upon completion of the reaction, the pyridine was evaporated off, and was washed with about 50 mL of methanol. The solution was then dried for 10 h at 50°C under reduced pressure to obtain 14.5 g of brown powdered product. The acid substitution level of this product was 2.36, as determined by elemental analysis.

#### Application Example 1 Oil foundation

(Component)	(wt%)
(1) Titanium oxide	14.0

(2) Mica	3.0
(3) Colorant pigment	3.0
(4) N-acetylglucosamine stearate	
(sample (1) manufactured in the reference examples)	16.0
(5) Cetyl octanoate	20.0
(6) Liquid paraffin	44.0

#### Preparation method

Components (1)-(3) were mixed, and then milled until uniform. A mixture of component (4) and components (5) and (6) was then heated and dissolved, and while cooling, the above milled material was added, and was kneaded thoroughly to effect uniform dispersion. The material was then poured into a container, thereby loading it to produce an oil foundation.

#### Comparative Example 1 Oil foundation

With the exception that starch-fatty acid ester was used instead of the oil gelling agent of component (4) in Application Example 1, an oil foundation was obtained in the same manner as in Application Example 1.

The oil foundations obtained in Application Example 1 and Comparative Example 1 above were used in practical testing, and a comparative evaluation was carried out. The results are presented in Table 1 based on the evaluations and evaluation standards presented below.

#### Evaluation standards

⊙: Extremely favorable

O: Favorable

Δ: Somewhat poor

X: Poor

Table 1

	Application Example 1	Comparative Example 1
Smoothness	⊙	O
Tack	⊙	O
Spreading	⊙	O
Degree of filmy feel	⊙	x
Cosmetic affixing properties	O	O

As is clear from the results of Table 1, the oil foundation of Application Example 1, which was a product of the present invention, had no tack and a smooth feel relative to the oil foundation obtained in Comparative Example 1. The spreading properties were also favorable, and there was no filmy feel after application of the cosmetic. Moreover, the cosmetic affixing properties were favorable, and thus a product was obtained that was superior in terms of both feel and properties when used.

Application Example 2 Paste-form lipstick

(Component)	(wt%)
(1) Titanium mica	10.0
(2) Colorant pigment	7.0
(3) Chitosan hydrolysis product palmitate	

(sample (3) manufactured in the reference example)	25.0
(4) Microcrystalline wax	7.0
(5) Cetyl isooctanoate	20.0
(6) Triisostearic acid glyceride	31.0

#### Preparation method

Components (1) and (2) were mixed and milled until uniform. Components (3)-(6) were mixed, and were heated and dissolved, whereupon the above milled material was added during cooling, and the mixture was thoroughly kneaded until uniform. The material was then poured and loaded into a container to prepare a paste-form lipstick.

The resulting paste-form lipstick of the present invention obtained in this manner had no tack, and also had a smooth feel. The lipstick also had favorable spreading properties, and thus exhibited favorable feel and properties when used. The material also had favorable stability.

#### Application Example 3 Gel-form eye-shadow

(Component)	(wt%)
(1) Mica titanium	25.0
(2) Iron oxide mica titanium	15.0
(3) Colorant pigment	5.0
(4) Glucosamine stearate	
(sample (2) manufactured in the reference examples)	30.0
(5) Liquid paraffin	10.0
(6) Tristearic acid glycerin	15.0

#### Preparation method

Components (1)-(3) were mixed and milled until uniform. Components (4)-(6) were then mixed, and after heating to dissolve them, the above milled material was added while cooling. The components were then thoroughly kneaded until uniform. Next, the material was poured and loaded into a container to produce a gel-form eye shadow.

The gel-form eye shadow of the present invention obtained in this manner had a smooth feel, and allowed formation of a light cosmetic with good adhesive properties. The cosmetic thus had favorable feel and properties when used, while also having favorable stability.

#### Application Example 4 Eye stick

(Component)	(wt%)
(1) Squalane	29.5
(2) Triisostearic acid glycerin	30.0
(3) Lanolin	10.0
(4) Macadamia nut oil	5.0
(5) N-Acetylglucosamine stearate	
(sample (1) manufactured in the reference examples)	25.0
(6) Vitamin E acetate	0.5

#### Preparation method

Components (1)-(6) were mixed and heated until dissolved, whereupon the mixture was poured and packed into a container, thus molding it to prepare an eye stick.

The eye stick of the present invention obtained in the manner described above had no tackiness and a smooth feel. The eye stick thus had favorable feel and properties when used, while also having a favorable molded condition and good stability.

#### Effect of the present invention

As described above, the cosmetic of the present invention contains a sugar-fatty acid adduct as oil gelling agent. Consequently, because the cosmetic lacks tack and has a favorable smooth feel, but does not produce a filmy applied cosmetic layer, the cosmetic of the present invention can be prepared as a gel-form or solid-form product that has superior feel and properties. Moreover the cosmetic also has favorable shape retention properties and stability. The present invention can thus offer a superior cosmetic with higher product quality than in the past.